

OXYGEN DETERMINATION AND STOICHIOMETRY OF SOME COALS

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INTRODUCTION

Chemical coal analysis is divided into two categories -- the Proximate and the Ultimate. In the Proximate Analysis one determines and reports "Moisture", "Ash", "Volatile Matter", and "Fixed Carbon". In the Ultimate coal analysis one actually determines the concentration of hydrogen, carbon, nitrogen and sulfur, reports in weight percent and estimates a quantity called "Oxygen by Difference" by subtracting the sum of the above elements plus the "Ash" from hundred. (1,2,3,4,5)

In addition, (1,2,3) the coal chemist distinguishes and attempts to determine three types of sulfur in coal (the sulfate sulfur, the pyrite sulfur, and the organic sulfur), and also tries to determine, or, at least, estimate, the Mineral Matter as originally present in coal. Chlorine, as well as several trace elements, especially those that can affect the environment (Hg, Cd, Pb, As, Se, Zn, etc.) are often also sought.

When we examine the nature of coal analysis reporting, we notice that in the Proximate category only the term "Moisture" may be equated with a chemically defined composition, namely, that of water. However, should this "Moisture" contain hydrocarbons or nitrogen volatilized at the drying temperature, then a simple weight loss method would not be sufficient to give chemically meaningful values. Thus we must describe and treat this "Moisture" (when so determined) as "weight loss" after drying in an oven at a given temperature for a certain time.

The quantity called "Ash" or "High Temperature Ash" (HTA) constitutes the total weight of incombustible residue derived from the inorganic mineral matter through dehydration, decomposition, oxidation and alteration caused by high temperature ($\sim 900^{\circ}\text{C}$) ignition of the coal in air. It is then a mixture of a heterogeneous character and is of an indeterminate and varying composition which is in some way related to the original bulk of minerals in coal. Subtracting the Total Ash in the Ultimate Coal Analysis in order to estimate the "Oxygen by Difference" introduces, therefore, indeterminate errors into otherwise stoichiometrically quite acceptable procedure of subtracting a sum of determined major elements from hundred in order to estimate the completeness of the analysis and assuming that the difference should be oxygen. One should also bear in mind that any method based on calculation by difference results in reflection of all errors in such a value.

From the standpoint of oxygen stoichiometry, the other two quantities of the Proximate Coal Analysis -- the "Volatile Matter" and the "Fixed Carbon" are of little importance because the first gives the bulk volatilized matter minus "Moisture"; the second is derived by subtracting the sum of the other three quantities ("Moisture" + "Ash" + "Volatile Matter") from hundred.

In order to attempt to quantitize the coal analysis further, we need thus a direct determination of oxygen, and once we have data for total oxygen, we must attempt to restructure the recalculation of coal analysis into a stoichiometrically more meaningful form. When this is done, the Material Balances of coal analyses should become more meaningful to the chemist and the engineer. The inadequacies of the chemical coal analysis recalculations and of the attempts to derive

from these stoichiometric data, as well as the need for a direct oxygen determination have been long recognized. We quote W. H. Ode of the U. S. Bureau of Mines (1963)(6): "The disadvantage of such an indirect method is that all of the errors of the other determinations are placed on the oxygen, and a Material Balance (emphasis ours) cannot be obtained to aid in checking the accuracy of the Ultimate Analysis".

Once a direct determination of oxygen is made, the coal analyst has to reconsider the standardized methods (3,4) of reporting and calculation of coal analysis. For example, the comparison of "oxygen determined" to "oxygen calculated by difference", using the standard methods, can be meaningless as Given (1975) has rightly pointed out (p. 9)(5) referring to the work of Hamrin, et al (1975) who have used a fast-neutron activation method similar, but not identical to ours to determine oxygen in Kentucky No. 9 coal (7). (See work by James, et al (1976)(16), Chyi, et al (18) and Block and Dams (17)).

We have suggested in 1974(8) the use of the ultra accurate fast-neutron activation method in coal analysis. Such method was first developed by Volborth and Banta in 1963 (9) for the analysis of rocks, lunar samples, and industrial materials (10,11,12). We have further perfected and adapted this method to the analysis of coal ash (13), coal (14), and the computerized recalculation of Material Balances (15) of six subbituminous Wyoming coals. This paper discusses specific problems we have encountered and presents new data on a wide variety of coals submitted by the Pennsylvania State University (Dr. Alan Davis) from the well characterized collection from an ERDA supported, computerized data bank (5) and some by the Illinois State Geological Survey (Dr. Harold J. Gluskoter and Dr. Rodney R. Ruch). We also utilize the data on the subbituminous coals from Wyoming (15) described earlier.

EXPERIMENTAL

The method used has been described in detail elsewhere (8,9,10,11,12,14). It consists of 20 seconds irradiation and 20 seconds counting of two samples, a standard and the unknown, simultaneously. A special feature of our system is the alternate switching of samples into opposite transfer channels to correct for electronic drift and bias. The nuclear reaction $^{16}\text{O}(n,p)^{16}\text{N}$ and counting of the resulting 6.1 and 7.1 MeV gammas with a half life of 7.3 seconds are used. The coal samples are packed into plastic containers (rabbits) and are sealed. Moisture at 105°C is determined on all samples, and the addition or loss of weight occurring while the samples are being packed is also determined by keeping a small sample exposed to ambient conditions for the duration of exposure. Some dried coal powders are very hygroscopic, gaining from 0.2 to .6% in weight during the 10 to 15 minutes of the packing procedure. Oxygen is determined on homogenized just opened "as received" samples on which moisture is determined in our laboratory at the time of packing. Oxygen is also determined on the dried samples (105°C). The precision of this method is $\pm 0.2\%$ (absolute) or better. A simple computer program computes the oxygen percentage in "as received" and in dried samples taking the determined moisture as H_2O into account. These data are input into a larger computer program which uses also data provided by the laboratory submitting the samples. These include the data of the Proximate and the Ultimate Coal Analysis. This program recalculates, using the ASTM Standard formulas (1,2,3), the coal analyses data based on our "Moisture", and gives the corresponding data on "Dry" and "Dry-Ash-Free" (DAF) basis. The result is four columns of analytical data on a coal sample, including the source data recalculated to our Moisture basis (See Table 1). The printout includes "Oxygen by Difference" calculated in each column and Oxygen Determined on "As Received" sample as well as on sample dried at 105°C. The determined oxygen is recalculated based on the total coal analysis data so that it can be compared in each column with the corresponding oxygen based on other methods of reporting of coal analyses.

The experiment is so designed as to permit the chemist to detect and estimate the minimum extent of oxidation of the coal in air during the Moisture determination at 105°C. This is done by comparison of determined versus back-calculated data on both samples in "As Received" and "Dry" columns.

Assuming that no other losses than water and no oxidation occur, the determined oxygen in the "Dry" column should closely correspond to the calculated based on oxygen determined in the "As Received" sample. If the oxygen in the mineral matter or, if unavailable, of the ash has been also determined or estimated properly and the analyses of C, H, S, N and Cl are accurate, a good sum should then be an indication of completeness of such a coal analysis. Higher oxygen determined in dry sample than that calculated based on "As Received" column should indicate oxidation or evolution of non-oxygen bearing gases (retention of more oxygen than was assumed). These processes could also balance out so that while no apparent weight loss occurs, oxidation and evolution of N_2 , CO_2 , CH_4 , C_2H_6 etc. has taken place. The correctness of the assumption that all moisture is water can thus be checked only approximately for each coal as analyzed. It must be understood that oxidation of coal parallel with a water loss would tend to result in too low values for "Moisture" and depletion of the system of that quantity of hydrogen associated with H_2O . Low reporting of "Moisture" does also result in too high calculated values for C, H, S, and N, and, therefore, in too low "Oxygen by Difference" values causing too high summations if oxygen content is determined independently. All of these effects have a tendency to increase the oxygen content in the dried coal. Thus in most coals, one would expect an increase in determined oxygen in oven dried samples.

Decreases of oxygen content in dried coal (after the weight loss has been accounted for as water) could be due to removal of surface oxygen and replacement of it by nitrogen or coal-derived methane, for example. This effect should be mostly negligible, especially since most coal would tend to oxidize at least somewhat during heating in air, masking this phenomenon.

RESULTS AND CONCLUSIONS

Thirty-three coals ranging in rank from Lignite to Bituminous coals and including subbituminous, high volatile, medium volatile and low volatile bituminous coals were analyzed and their analyses recalculated in the manner described above.

To illustrate the behaviour of these coals upon drying, the deviations between oxygen in "Dried" versus "As Received" samples were plotted in Figure 1.

Compared on DAF basis, seventeen (17) of these coals show oxygen content higher when determined in the oven dried coal (105°C) than that recalculated to this basis from oxygen determined on "As Received" (by us) coal. In twelve (12) coals no change within the precision limits of $\pm 0.3\%$ absolute could be observed and in four (4) coals oxygen contents lower than the precision limit were detected. Thus only about 12% of all coals analyzed showed effects of some process that may be called reduction, whereas 52% of all coals analyzed showed detectable oxidation and about 36% showed insignificant changes undetectable by our method. This confirms the predicted behaviour in the last paragraphs of the previous chapter. Oxygen loss in the dried coal at 105°C is unlikely because most of the processes that can occur concurrently would tend to oxidize or increase the oxygen content if the gases evolved do not contain or contain less oxygen than the water as assumed. Only molecular oxygen if driven off the surface would cause a decrease of overall oxygen in the dried coal. It is clear that there is a positive bias in this comparison as seen in Figure 1 and that it is not dependent on the rank of coal.

A typical recalculation of two coal analyses derived from computer printouts is given in Table 1. The first analysis is of a High Volatile A Bituminous Coal

TABLE 1
OXYGEN DETERMINATION BY FAST NEUTRON ACTIVATION ANALYSIS IN COALS
RECALCULATED ANALYSES

PROXIMATE ANALYSIS	HVA BITUMINOUS COAL, WEST VIRGINIA, PSOC-121			LIGNITE, TEXAS, PSOC-140		
	AS REC'D	DRY	DAE	AS REC'D	DRY	DAE
% MOISTURE	1.29 ±0.1*			33.96 ±0.1*		
% ASH	1.57	2.55		6.19	9.37	
% VOLATILE	27.89	38.38	39.39	29.58	44.81	49.45
% FIXED CARBON	58.31	59.07	60.61	50.26	45.82	50.55
SUMMATIONS	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS						
% HYDROGEN	5.65 *1	5.57	5.72	6.91*1	4.71	5.20
% CARBON	81.16	82.22	84.37	42.35	65.01	71.72
% NITROGEN	1.72	1.75	1.79	0.75	1.14	1.26
% ORGANIC SULFUR	0.93	0.94	0.97	0.45	0.65	0.71
% OTHER SULFUR	0.27	0.27	0.00	0.71	0.32	0.00
% OXYGEN (BY DIFF)	(7.75)	(6.68)	(7.15)	(45.58)	(18.80)	(21.10)
% O (BY ENAA) AS IS	9.18 ± .04*	8.14	7.15 *2	47.34 ± .15*	46.01	42.95 *2
% O (BY ENAA) DRIED	8.17 ± .04	8.13 ± .07*	7.14	48.05 ± .15*	27.06 ± .13*	25.10
SUM INC. ENAAO (AS IS)	99.03	99.02	100.13	98.59	97.87	102.88
SUM INC. ENAAO (DRIED)	99.02	99.01	100.12	99.28	98.91	104.08
% CATIONS, ETC., AS ASH	1.36 *3	1.38	0.00	3.34 *3	5.06	0.00
SUMMATION (AS IS)	100.15	100.15		101.55	103.35	
SUMMATION (DRIED)	100.14	100.14		102.24	103.39	

* DETERMINED BY US. *1 INCLUDES H FROM MOISTURE *2 EXCLUDES ESTIMATED OXYGEN IN ASH

*3 ESTIMATED AS 54% OF ASH CONTENT *4 BASED ON MOISTURE CONTENT

TABLE 2

DIFFERENCES BETWEEN OXYGEN BY DIFFERENCE AS REPORTED IN CLASSICAL COAL ANALYSIS AND OXYGEN DETERMINED BY NA AND OXYGEN RECALCULATED, ASSUMING ASH CONTAINED 46% O

COAL NO.	% AS DIFF. REPORTED U.S.B.M. "AS RECEIVED"	O DETD NA	O DIFF CALC (ASH 46% O)	% ASH
K-46566	36.6	42.34	44.34	7.70
K-46218	32.3	35.90	37.82	5.50
K-46217	31.7	36.15	37.89	6.20
K-46216	33.2	36.85	38.13	4.90
K-46565	38.8	43.28	44.19	5.40

from the Tioga Seam, Tioga No. 1 Mine, Nicholas County, West Virginia (PSOC-121). In this analysis the moisture determined in our laboratory (1.29%) is within .2% of the moisture reported (1.52%) in the Source Data (Pennstate University), the Ash is low (2.52%) and most of the sulfur is organic. Both these factors assure that the errors due to the fact that ash is not mineral matter will be small. Indeed, this analysis balances well, the oxygen based on direct determination in coal "As Received" by us as well as oxygen determined on dried coal at 105°C corresponds closely. Thus we can say that this coal does not oxidize perceptibly during drying in air and that the moisture is probably all water (H_2O). Having not analyzed the ash, we estimate that it contained 46% oxygen, as shown by us (13) for U.S. coals and by Block and Dams (17) for some European coals. Thus it must contain 54% cations including sulfur and chlorine, and we add this amount to the summations which are first derived by adding the determined C, H, N, S, and total O (determined by FNAA). The good second summation shows that in this coal our assumptions and approximations were justified.

The second compilation is of a Lignite from the Darco Mine, Harrison County, Texas, PSOC-140. Determined moisture (33.96%) compares closely with that reported by Pennstate (33.39%). The oxygen determined in the dried coal (105°C), however, is 1.05% (absolute) higher than would be expected based on recalculated oxygen based on oxygen determined in the "As Received" coal. This indicates considerable oxidation and possibly evolution of gases containing less oxygen than water. This coal contains relatively little pyrite sulfur (.21%) and only 6.2% ash, so that the estimated 54% cations plus sulfur plus chlorine may be used to approximately balance the analysis when the determined oxygen values are summed up in the DAF column. Since we know that this coal has oxidized by addition of approximately 1.05% O (absolute), we can assume that the "Moisture" loss should have been reported higher by at least that amount. Assuming that all other determinations were done correctly, the use of the too low Moisture value would result especially in proportionally too high calculated value for C, H, N, and S, and thus too low values for O by Difference, which seems to be the case. This can be seen by comparison with the determined oxygen in "as received" coal calculated to DAF basis. When this oxygen value is used in the summation, one may approximately estimate whether the state of the complete coal analysis as reported is satisfactory. In this case, a bulk error of roughly about 3% is indicated. It can be due to a combination of interrelated factors, which can be a cause for erroneous moisture determination, each to a different degree. These are: a) oxidation during moisture determination; b) evolution of gases other than H_2O containing none or less oxygen than water (N_2 , CO , CO_2 , CH_4 , C_2H_6 , etc.); c) calculation errors based on faulty moisture determination which may cause a dilution effect especially on the major components, such as the carbon value, for example; d) analytical errors and bias; e) the fact that ash is not mineral matter and that pyrite sulfur should be counted as pyrite, FeS_2 , as Given has pointed out (5)(pp. 31-33).

The treatment of the coal analyses described above raises several critical questions, of which only the most important can be discussed here. A few assumptions have been made above which strictly speaking are not true, and once one attempts to quantitize the coal analysis, then why not proceed logically by removing all approximations and report on a stoichiometric basis?

It turns out that this cannot be done in one step without demolishing a century-old convention due to the complex nature of computations of the classical coal analysis. The basic reason for the way a coal analysis is computed today is the variable nature of the coal substance and the inability of the coal chemist to procure a rapid and inexpensive oxygen analysis within the Ultimate Analysis Family. This situation has resulted in efforts to somehow bypass this dearth of information and turn out computations which would approximate the true chemical stoichiometric balances in the composition of coal as closely as possible. In short, the coal chemist has accepted the value for "Ash" as representative of the

mineral matter in the "As Received", the "Dry" and the derivation of the "DAF" columns. Also, in the calculation of the "Oxygen by Difference", the whole Ash is customarily deducted from hundred. Obviously, by definition, one cannot equate this quantity with oxygen determined directly and a quick comparison in Table 2 shows that such correlation can lead to gross errors and misunderstanding. Nevertheless, inadvertently such comparisons are often made especially in industry. This is presently the rule, and worse, when "Oxygen by Difference" is used to plot such ratios as H/C versus O/C (19,20) where by implication and the use of the chemical symbol, a very misleading picture is given.

In Table 2 we have compiled "Oxygen by Difference" data as reported by the U.S. Bureau of Mines on "As Received" basis (first column) with oxygen determined by FNAA on samples as received by us and back-calculated based on our moisture data (second column) with oxygen by difference calculated in our computer program assuming that the ash contained 46% O (third column) and subtracting only the oxygen of the ash. While comparison of the conventional "Oxygen by Difference" with oxygen determined makes little sense, this column shows improvement in terms of comparison of oxygen by difference so calculated with the determined oxygen. We seem to be thus on the right path, and able to see whether the overall assumptions were correct.

The ash portion of coals varies from a few percent to about 20 percent and more. To correct for the inadequacy of reporting and subtracting as such, Parr in 1932 (21) has proposed to estimate the Mineral Matter by the formula: % Mineral Matter = $1.08 \times \% \text{ Ash in Coal} + 0.55\% \text{ Sulfur in coal}$, where the factor 1.08 is the empirically derived value for water of hydration of the minerals usually found in ash.

Based on similar consideration, King, et al in 1936 (22) have derived a more accurate Mineral Matter (MM) calculation formula: % MM = $1.09 \times \% \text{ Ash} + 0.5 \times \% \text{ Pyritic S in Coal} + 0.8 \text{ CO}_2 \text{ in Coal} - 1.1 \times \% \text{ SO}_3 \text{ in Ash} + \% \text{ SO}_3 \text{ in Coal} + 0.5 \times \% \text{ Cl in Coal}$.

These formulas have been derived from accurate stoichiometric relations considering decomposition of hydrated minerals, oxidation and formation of Fe_2O_3 from FeS_2 , etc. The stoichiometry and accuracy of Mineral Matter Evaluation can be further improved by reconstituting the main minerals based on the analysis of ash. These are kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and pyrite, FeS_2 , as shown by Rees (2).

The fourth column of Table 2 compares the ash contents of the coals. In our stepwise approach to the stoichiometric interpretation of coal analysis, we have found improvement if we estimate the composition of the ash. Obviously this is only an approximation and, as pointed out by Given (5), one should better use the DAF column where the influence of the mineral matter content, sulfur, and ash is further minimized. One could assume according to Parr (21) that mineral matter contains about 8% H_2O , or 9% according to King, et al (22), in which case our calculated oxygen by difference should become somewhat lower because oxygen of the water of hydration in the mineral matter should also be subtracted. Indeed, in all our cases, we obtained a better agreement with determined oxygen if this is done. All of these coals have a relatively low ash content, but nevertheless, the overall effect is about .5% less Oxygen. Taking sulfur in ash into account should further improve the agreement. Thus in many coals one may need only a recalculation of ash according to the mineral matter formulas to check stoichiometry and balance the summations. Oxygen determination gives us thus important information in characterizing coals. It may help to point out rapidly any unusual mineral composition or oxidative behaviour. Coals, where oxygen by difference value calculated by subtracting not the whole ash but only the corresponding quantity of oxygen calculated by the Parr formula agrees closely with oxygen determined, where summations balance out, may be regarded as sufficiently characterized. In

pyrite-sulfur-rich coals and coals with carbonates or unusual components, the more complex formula by King, et al (22) may be used. Where neither of these formulas produce a good balance, more detailed chemical work is indicated. As pointed out by us before, oxygen analysis in coal ash characterizes also the mineral matter and gives useful information on the total of all other constituents including S, Cl, etc., in ash (13).

Considerable effort has thus been spent to interpret the ash and from it the mineral matter portion of coal. One may ask why spend so much effort to evaluate a relatively minor segment of coal analysis in order to achieve stoichiometry as long as a major constituent -- oxygen -- remains undetermined. Obviously the coal chemists have done everything in order to approach true stoichiometry and be able to interpret the chemistry of coal and report the analyses in as balanced a form as possible.

We propose, therefore, that adding direct oxygen determination to coal analysis as we have done, and furthermore, determining the oxygen content in ash should bring us closer to the true stoichiometric interpretation of coal analysis. From the computer printouts of the 33 coals we have analyzed for oxygen, we can see that a single oxygen determination in a coal "As Received" quite accurately characterizes the coal as to rank, and that once the normal carbon to oxygen ratios are established for a wide variety of coals, major deviations, due to high pyrite-sulfur content or unusual mineralogy can be easily spotted (see Figure 2). This plot was obtained from the 33 recalculated coal analyses.

We distinguish stages or steps of progressively more correct approach to stoichiometric quantitation and recalculation of coal analysis. The first step is to analyze the "As Received" and "Oven Dried" coal at 105°C for oxygen and to estimate the oxygen in Ash based on former work (13,17), which shows that in a great variety of normal coals, oxygen in ash varies between 44 and 48 weight percent. In 29 calculated analyses out of a total of 33 plotted, this assumption is indeed meaningful. Reasonably good summations and balances are so obtained (see Figure 1 and Table 3), except for coals with 2 to 8% S.

Secondly, When an actual oxygen analysis on ash corresponding to the coal analyzed is performed, the data should balance somewhat better. Any unusual deviations in the oxygen content of the high temperature ash would then be a signal necessitating closer scrutiny and checks of the type of mineral matter. This approach provides a better approximation, giving us more information because actual accurate oxygen determination in coal ash furnishes us with an exact sum of the cations plus sulfur and chlorine in that ash. This means that better and more meaningful summations will result. This work is in progress.

Thirdly, to proceed further toward yet better stoichiometric balance, one can either calculate the mineral matter by the Parr formula (21), or better, by the King (22) formula as stated above. For this, however, one needs to determine total sulfur in coal in the first case, and an analysis for pyrite sulfur, CO₂, Cl, and SO₃ in coal, and SO₃ in ash and, if the content of kaolinite, pyrite and SiO₂ is to be calculated, also an analysis of ash for Al₂O₃, SiO₂, and S.

Because such a chemical approach is time consuming, and not entirely satisfactory, one may for our purposes better determine the Mineral Matter by preparing the so-called Low Temperature Ash (LTA) from the coal as proposed by Gluskoter in 1965 (23) and used by O'Gorman and Walker in 1971 (24) and further refined by Fraser and Belcher in 1972 (25) and Kinson and Belcher in 1975 (26). This method consists of radio frequency ashing of coal at temperatures of 1000° to 1500°C and appears to give results which are perhaps the closest approximation to the true Mineral Matter in coal on "As Received" or "Dry" basis. Mineralogy of LTA ash has been recently (1976) studied by Mitchell and Gluskoter (27). An analysis of oxygen

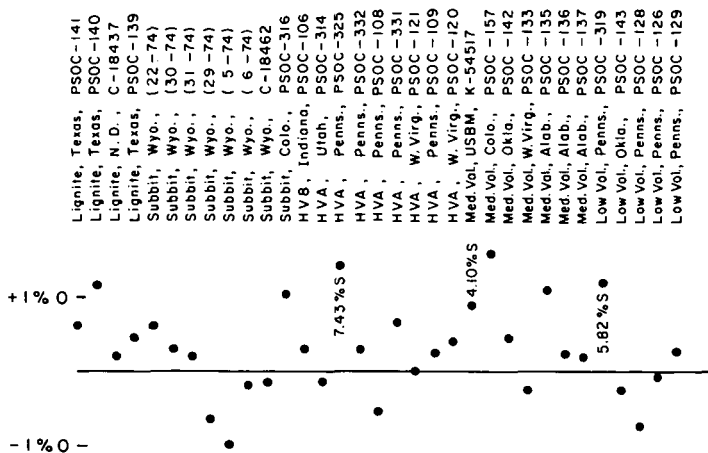


FIGURE 1. PLOT SHOWING INCREASES AND DECREASES OF OXYGEN IN 33 COALS WHEN DRYING AT 105°C. % O DRY COAL MINUS % O AS RECEIVED COAL. NOTE SULFUR-RICH SAMPLES.

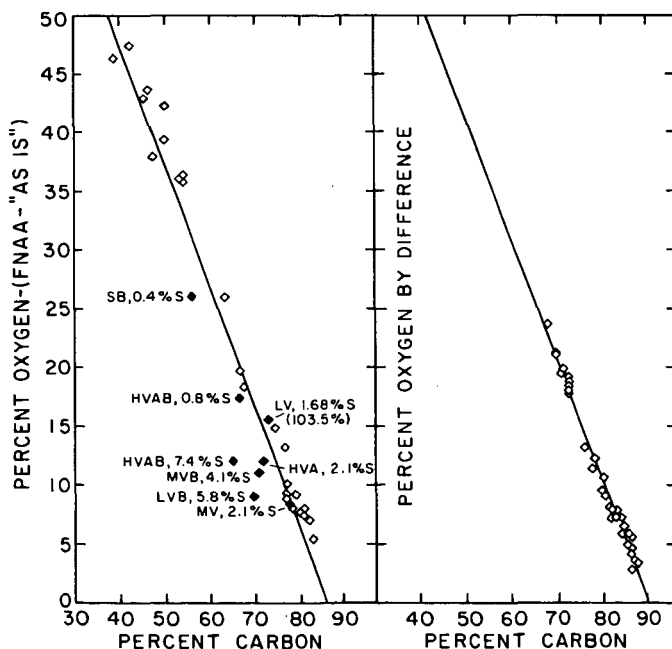


FIGURE 2. D/C PLOT OF 33 COALS ON "AS RECEIVED" BASIS USING OXYGEN VALUES DETERMINED BY FNAAS, AND "BY DIFF".

in Low Temperature Ash has been performed by us on two samples (13), however, so far we have not been able to obtain the corresponding coals. In sulfide rich coals, since pyrite is not oxidized during LTA procedure, the large error caused in the Oxygen by Difference estimation in all columns for the coals PSOC-325, PSOC-319, K-54517, in Table 3, would be minimized, if oxygen were determined directly in LTA ash. A similar approach has been taken by Hamrin, et al in 1975 (7). Assuming that the minerals in coal are not destroyed by radio frequency heating, this approach if combined with oxygen analysis in coal on "As Received" and "Oven Dried" basis as done by us may be the best way of determining the true "Organic Oxygen" in coal. We are now installing the necessary equipment in order to be able to further investigate this question.

Given and Yarzab (pp. 31-33) (5) have in 1976 emphasized the inadequacy of the ASTM Standard D 3180 reporting in sulfur-and mineral-matter-rich coals and propose the use of the British Standard 1016 Part 16 corrected procedure which distinguishes organic sulfur and recalculates the percentage of pyrite in mineral matter based on the pyrite sulfur. This is a better approach stoichiometrically as can be seen from the comparison of data given by these authors (ibid p.32). We have used at this stage the ASTM Method (see Table 3) which reports the total sulfur subtracting it from hundred on the "Dry" basis. We find that the "Oxygen by Difference" value if calculated by the British Standard Method adopted by the Pennsylvania State University agrees indeed much better with our determined values for oxygen. Therefore, where data on the type of sulfur were available, we have distinguished organic sulfur and included it in the DAF column, but have excluded the sulfate and pyrite sulfur in coal. We realize that even this approach is not fully satisfactory and intend to introduce the exact procedure recommended by Given.

In Table 3 we have compiled our data based on Pennstate data on DAF basis. Twenty-five analyses of coals not reported by us elsewhere are given. The coals are plotted in sequence based on increasing Fixed Carbon content. To save space, information on Moisture as originally reported, and as determined by us, as well as the percent Ash as reported on "As Received" basis are given in parentheses under Proximate Analysis, but do not figure in summations. These data permit the reader familiar with coal analysis and classification to make meaningful comparisons. The varying ash content is also an important criterion of accuracy expected in comparison of "oxygen by difference" with actual "oxygen determined", especially in sulfur-rich coals. In the Ultimate Analysis columns "Other Sulfur" when available is given also in parentheses, but not summed, because, as one can see in coals PSOC-325, K-54517, PSOC-137 and PSOC-319, our method permits one to estimate the approximate sulfur content based on summations. Note the retention of sulfur in carbonate-rich coal's ash(13).

It can be seen that "oxygen by difference" on DAF basis agrees reasonably well with determined oxygen in all coals that do not contain sulfur. Coals with high ash content but low sulfur also tend to balance reasonably well (see PSOC-106). Low ash coals in general give better summations (as expected) than high ash coals. The presence of high sulfur masks the effect of high ash and causes low summations if oxygen is determined. Good agreement between "oxygen by difference" and determined oxygen for "As Received" and "Dried" coal seems to indicate a well balanced analysis and minimal oxidation effects upon drying. Differences in the two determined oxygen categories tend to be mostly due to oxidation and evolution of other gases than H_2O , and, therefore, also point toward an erroneous Moisture determination due to the canceling effect of oxidation when based on weight loss.

The data on sulfur-rich coals seem to indicate that much of the sulfur, even though reported as "other" or "sulfide" sulfur is in some way bound to the coal molecule with the sulfur replacing oxygen. A part of the "inorganic sulfur" appears to compete for oxygen sites in coal in some way because all sulfur-rich coals analyzed show relatively much lower determined oxygen concentration in the

TABLE 3
OXYGEN DETERMINATION BY FAST NEUTRON ACTIVATION ANALYSIS (FNAA) IN COALS
RECALCULATED ANALYSES

PROXIMATE ANALYSIS		C18437	PSOC-139	C18462	PSOC-141	PSOC-314	PSOC-325	PSOC-316	PSOC-108	PSOC-332
%	MOISTURE (SOURCE)	(6.80)	(30.29)	(5.90)	(33.16)	(4.08)	(2.86)	(12.12)	(1.41)	(5.65)
%	MOISTURE (DETD)	(7.98)	(21.06)	(5.48)	(22.14)	(4.07)	(1.30)	(12.88)	(1.62)	(3.81)
%	ASH	(9.40)	(10.70)	(9.56)	(6.03)	(9.63)	(15.76)	(4.55)	(9.37)	(13.08)
%	VOLATILE	51.07	50.89	50.39	49.15	47.91	44.68	40.97	41.31	41.42
%	FIXED CARBON	48.93	49.11	49.56	50.85	52.09	55.32	59.03	58.69	58.55
SUMMATIONS		100.00	100.00	99.95	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSIS										
%	HYDROGEN	5.11	5.59	5.42	5.25	6.11	5.64	5.52	5.57	5.86
%	CARBON	69.56	72.29	72.66	71.70	80.25	80.72	73.36	82.90	82.37
%	NITROGEN	0.33	1.30	1.50	1.35	0.63	1.41	2.30	1.22	1.61
%	ORGANIC SULFUR	0.79	0.76	1.02	0.74	0.66	0.00	0.48	1.21	0.21
%	OTHER SULFUR	(0.20)	(0.08)	(0.40)	(0.10)	(0.16)	(7.43)	(0.07)	(2.08)	(0.83)
%	OXYGEN (BY DIFF)	(23.62)	(20.03)	(19.40)	(20.97)	(11.35)	(12.23)	(13.14)	(9.10)	(9.45)
%	O (BY FNAA) AS IS	25.17	19.61	21.13	23.19	11.87	4.29	15.04	7.09	9.49
%	O (BY FNAA) DRIED	25.04	22.09	20.97	23.83	11.73	5.82	16.08	6.55	9.78
SUM	INCL FNAAO (AS IS)	101.55	99.58	101.73	102.24	100.53	92.07	101.90	98.05	100.04
SUM	INCL FNAAO (DRIED)	101.32	102.06	101.57	102.88	100.39	93.59	102.94	97.52	100.33
PROXIMATE ANALYSIS		PSOC-106	PSOC-331	PSOC-109	PSOC-120	K-54517	PSOC-157	PSOC-137	PSOC-135	
%	MOISTURE (SOURCE)	(6.40)	(5.31)	(1.88)	(1.93)	(2.30)	(1.41)	(0.71)	(0.71)	
%	MOISTURE (DETD)	(3.60)	(4.73)	(5.75)	(1.46)	(1.53)	(5.09)	(1.74)	(0.81)	
%	ASH	(17.06)	(4.78)	(5.05)	(5.88)	(13.60)	(6.63)	(7.00)	(4.86)	
%	VOLATILE	49.91	49.87	47.82	44.00	28.66	26.63	26.43	21.85	
%	FIXED CARBON	50.09	50.13	52.15	55.99	71.34	73.37	73.57	75.15	
SUMMATIONS		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
ULTIMATE ANALYSIS										
%	HYDROGEN	5.52	5.62	5.50	5.12	5.04	5.18	4.82	4.93	
%	CARBON	82.76	83.97	84.62	85.44	85.73	89.11	86.97	88.28	
%	NITROGEN	0.55	1.62	1.29	1.54	1.43	2.36	1.53	1.47	
%	ORGANIC SULFUR	0.54	0.75	0.58	0.69	0.00	0.53	0.81	0.59	
%	OTHER SULFUR	(0.12)	(0.07)	(0.09)	(0.03)	(4.10)	(0.36)	(2.07)	(0.05)	
%	OXYGEN (BY DIFF)	(10.64)	(8.04)	(7.90)	(7.21)	(7.88)	(2.86)	(5.87)	(6.05)	
%	O (BY FNAA) AS IS	12.21	9.69	9.99	6.62	3.99	1.64	4.15	6.88	
%	O (BY FNAA) DRIED	12.51	10.34	10.24	7.04	4.88	3.23	4.35	6.47	
SUM	INCL FNAAO (AS IS)	101.60	101.64	102.15	99.50	96.20	98.82	98.30	99.60	
SUM	INCL FNAAO (DRIED)	101.91	102.30	102.40	99.92	97.08	100.42	98.30	100.70	
PROXIMATE ANALYSIS		PSOC-136	PSOC-142	PSOC-133	PSOC-319	PSOC-143	PSOC-128	PSOC-126	PSOC-129	
%	MOISTURE (SOURCE)	(0.63)	(0.94)	(0.76)	(1.85)	(0.88)	(1.24)	(0.64)	(1.67)	
%	MOISTURE (DETD)	(0.75)	(1.28)	(0.69)	(1.96)	(0.40)	(0.80)	(0.99)	(0.33)	
%	ASH	(2.40)	(10.88)	(6.05)	(15.30)	(3.74)	(13.40)	(6.93)	(16.33)	
%	VOLATILE	24.79	23.22	22.90	22.01	21.73	21.06	20.02	19.80	
%	FIXED CARBON	75.23	76.78	77.10	77.99	78.27	78.94	79.98	80.38	
SUMMATIONS		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
ULTIMATE ANALYSIS										
%	HYDROGEN	4.65	4.46	4.38	4.57	4.74	4.72	4.79	5.01	
%	CARBON	88.06	89.04	90.51	86.49	88.95	87.23	88.15	89.86	
%	NITROGEN	1.74	0.20	1.06	1.62	1.43	1.09	0.99	1.01	
%	ORGANIC SULFUR	0.58	0.70	0.60	0.10	0.63	0.45	0.48	0.45	
%	OTHER SULFUR	(0.02)	(0.42)	(0.02)	(5.82)	(0.07)	(1.83)	(0.63)	(0.31)	
%	OXYGEN (BY DIFF)	(4.97)	(5.60)	(3.44)	(7.22)	(4.19)	(6.51)	(4.63)	(6.88)	
%	O (BY FNAA) AS IS	5.79	4.06	3.86	0.52	3.62	10.04	4.01	3.68	
%	O (BY FNAA) DRIED	4.02	4.51	3.50	1.70	3.37	9.29	3.84	3.55	
SUM	INCL FNAAO (AS IS)	98.82	98.47	100.43	93.30	99.46	103.54	99.40	100.28	
SUM	INCL FNAAO (DRIED)	99.05	98.92	100.07	94.48	99.20	102.79	99.29	100.29	

DAF column than other normal coals. Thus, our method when further developed may help to evaluate the role of "Organic Oxygen" and "Organic Sulfur" in coal. We have started recalculations based on the Parr formula and the King formula to simulate the mineral matter closer in order to correct the DAF column for the effect of the additional oxygen associated with the hydrated portion of minerals. Such correction increases the proportion of C and N, and decreases somewhat the oxygen by difference values (as well as hydrogen). When this is done, more accurate "Sulfur by Difference" values can then be estimated from summations in Table 3. Thus, accurate oxygen determination permits us to estimate approximately the total sulfur when other components routinely determined in coal analysis are known. Oxygen determination in ash also aids in this case substantially, because if it is lower than the regular content ($46 \pm 2\%$ O) considerable sulfur or heavy constituents in ash may be indicated.

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